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Abiotic Reduction of Nitro Aromatic Pesticides in Anaerobic Laboratory Systems

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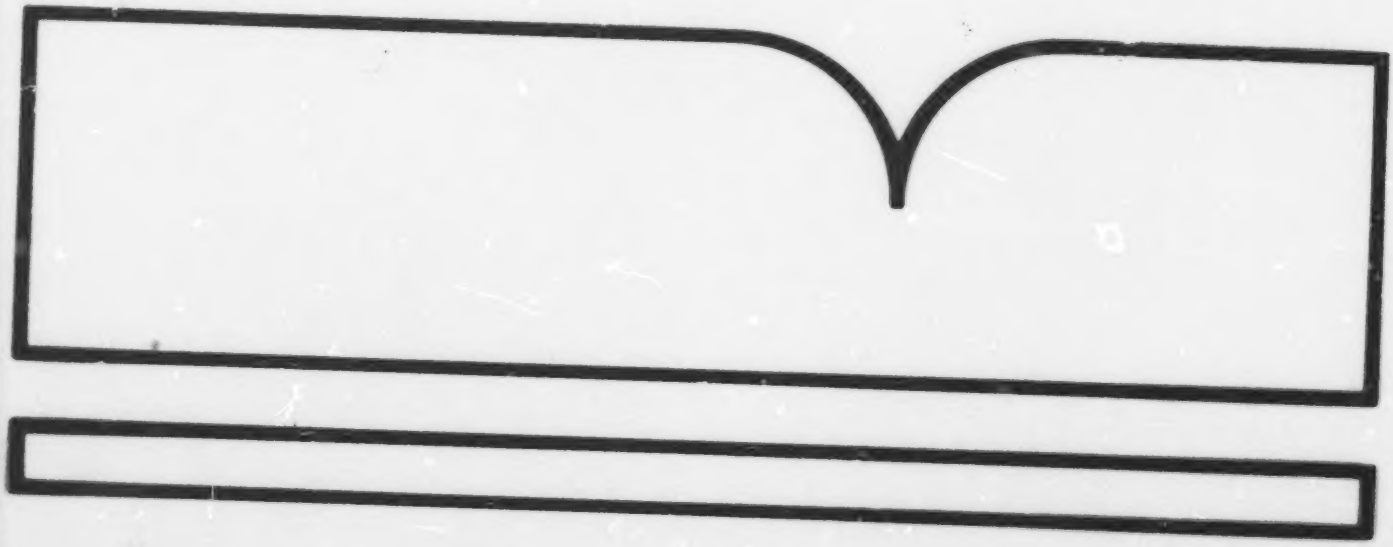

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16. ABSTRACT

Rapid abiotic reduction of nitro aromatic pesticides occurs in homogeneous solutions of quinone redox couples, which were selected to model the redox-labile functional groups in natural organic matter. The kinetics of methyl parathion disappearance are first order in methyl parathion and first order in the monophenolate form of the hydroquinone. The concentration of the monophenolate was calculated from electrode measurement of Eh and pH of the model system and the thermodynamic data. The second-order rate constant at 25°C is 31.1±4.9 L $min^{-1}mol^{-1}$ in a solution where the quinone-hydroquinone redox system consists of partially reduced indigo disulfonate and is (3.80±0.65) x 10^4 L $min^{-1}mol^{-1}$ in redox systems based on anthraquinonedisulfonate. Reduction of methyl parathion is negligible above about -50 mV; this is the apparent reduction potential of methyl parathion under the conditions used in this study. In indigodisulfonate model systems, the disappearance of profluralin is also second order but with a rate constant equal to 79.0±8.6 L $min^{-1}mol^{-1}$.

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Abiotic Reduction of Nitro Aromatic Pesticides in Anaerobic Laboratory Systems

Paul G. Tratnyek[1] and Donald L. Macalady*

Rapid abiotic reduction of nitro aromatic pesticides occurs in homogeneous solutions of quinone redox couples, which were selected to model the redox-labile functional groups in natural organic matter. The kinetics of methyl parathion disappearance are first order in methyl parathion and first order in the monophenolate form of the hydroquinone. The concentration of the monophenolate was calculated from electrode measurement of Eh and pH of the model system and thermodynamic data. The second-order rate constant at 25 °C is 31.1 ± 4.9 L min^{-1} mol^{-1} in a solution where the quinone–hydroquinone redox system consists of partially reduced indigo disulfonate and is (3.80 ± 0.65) × 10^4 L min^{-1} mol^{-1} in redox systems based on anthraquinonedisulfonate. Reduction of methyl parathion is negligible above about −50 mV; this is the apparent reduction potential of methyl parathion under the conditions used in this study. In indigodisulfonate model systems, the disappearance of profluralin is also second order but with a rate constant equal to 79.0 ± 8.6 L min^{-1} mol^{-1}.

Environmental reduction reactions of organic pollutants that may be abiotic include dehalogenation, nitro reduction, dealkylation, azo reduction, and sulfoxide reduction (Macalady et al., 1986; Sethunathan, 1973; Tsukano, 1986). Nitro reduction is the most easily effected and, we believe, the most likely to occur abiotically in the environment, so it was selected as the focus of this work. Nitro reduction of the phosphorothioate insecticides fenitrothion, methyl parathion, and parathion to their amino analogues is known to occur rapidly in anaerobic soils and sediments and is considered to be largely an abiotic process (Adhya et al., 1981a,b; Gambrell et al., 1984; Wahid et al., 1980; Wahid and Sethunathan, 1979; Wolfe et al., 1986). However, currently, the rate of abiotic nitro reduction in the environment cannot be predicted because the pathways and associated kinetics are not known.

Speculation regarding the agents responsible for abiotic reduction of organic pollutants most commonly emphasizes ferrous ion or complexes of ferrous ion (Macalady et al., 1986). However, it is a common generalization that natural organic matter is a strong reducing agent (Crosby, 1970; Stevenson, 1982; Thurman, 1985; Waite, in press), and organic matter will reduce metals that can, in turn, reduce organic pollutants. Presumably, organic matter can also reduce organic pollutants directly. Studies to date have not identified the reducing site(s) on natural organic matter though they are likely to be associated with polyphenols, especially those with para orientation, i.e. hydroquinones (Waite, in press). The reactions that we report here are all direct reductions of nitro groups to amines by hydroquinones.

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We have determined the effects of Eh, pH, and other reaction conditions on the kinetics of nitro reduction by hydroquinones. Despite the severe difficulties with measurement and interpretation of electrode potentials in natural materials (Bohn, 1971; Hostettler, 1984; Lindberg, 1983; Whitfield, 1969), they continue to be widely reported as qualitative indicators of redox conditions. Part of the environmental significance of this project derives from the use of measured electrode potentials as a predictor variable. However, in this work poised model systems are used rather than soil or sediment samples in part because potentiometry in comparatively ideal laboratory solutions is much more satisfactory than in natural materials. The model systems were homogeneous poised solutions based on quinone–hydroquinone redox couples.

EXPERIMENTAL METHODS

Model Redox Systems. A 5 mM aqueous solution of indigodisulfonate (used as received from Fisher, certified grade, and from Aldrich) was used as the basis of a model system in the manner described in Experimental Procedures. Similarly, anthraquinonedisulfonate (used as received from Aldrich) was prepared in 5 mM aqueous mixtures, but these were slightly cloudy. Gas chromatographs of the isooctane extract of the anthraquinonedisulfonate mixture showed a large impurity peak that was shown to be anthraquinone. The impurity peak was reduced but not eliminated by filtering all anthraquinone disulfonate mixtures at 0.22 μm. Subsequently, it was shown that anthraquinone had no measurable effect on the rate of reduction of methyl parathion. Model systems were also based on 5 mM solutions of quinhydrone (used as received from Eastman) and dihydroquinone (used as received from Mallinckrodt, photopurified grade, and Aldrich, Gold Label grade). Fulvic acid was extracted by the traditional alkaline/acid method from a black, sulfurous, organic-rich sediment collected at Chatfield Reservoir (Douglas County, CO).

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Experimental Procedures. All experiments were performed in an anaerobic chamber (modified Forma 1025) under an atmosphere of 5% H_2 in N_2. The 5 mM solutions of oxidized model system were reduced in a reductor, a device that consisted of a gas dispersion tube surrounded with 0.5% Pt- or Pd-coated $^1/_8$-in. alumina beads (Engelhard) in a short chromatography column. The column was filled with solution, and reduction was affected by bubbling H_2 over the catalyst. Measured quantities of the reduced and unreduced 5 mM solutions were combined to achieve the desired proportions of the two forms. Then, final adjustments in the conditions of the solution were made—with reference to electrode measurements of redox potential and pH—by titration with NaOH, HCl, and/or additional portions of the reduced or unreduced solutions.

Combination pH electrodes generally gave reproducible and stable measurements in the model system solutions. The reference cell used in redox potential measurement was Ag/saturated AgCl in 4 M KCl; however, all potentials reported herein have been corrected to the standard hydrogen electrode (SHE) scale. Several types of redox working electrodes were used: 6 mm × 150 mm wax-impregnated graphite (WIG) rods and Pt in the form of screens or gauze. The WIG electrodes were pretreated by polishing with wet 0.1-μm alumina powder followed by brief sonication and copious rinsing with water. The shapes of the Pt electrodes precluded polishing so they were washed in hot methanol and heated in a gas flame until glowing red. Working electrodes were not pretreated between every use but about every week and whenever there was a major change in the solutions contacting the electrodes. After indigodisulfonate and anthraquinonedisulfonate solutions were proven to give Nernstian electrode response (in part by taking advantage of the fact that oxidized indigodisulfonate is blue and the reduced form is yellow, so it is possible to verify the electrode measured Eh with potentials calculated from absorbance measurements), only the WIG electrode was used for routine work and the measured potentials are treated as Nernstian Eh's in Results and Discussion. However, as many as two WIG and three Pt electrodes were used for interelectrode comparison in systems like benzoquinone and fulvic acid that gave electrode response that was unreliable.

Studies of disappearance rates of nitro aromatic pesticides in the model systems were performed primarily using methyl parathion, but also with profluralin (both analytical reference standards from the U.S. EPA Pesticides and Industrial Chemicals Repository). After electrode measurements were made, substrate was added to the medium and aliquots were taken at appropriate times, the aliquot was extracted with isooctane, and the extract was analyzed for unreacted substrate by gas chromatography with electron capture detection (Hewlett-Packard 5890). Usually 0.7 μL of extract was injected in splitless mode at 180 °C. The column was a 25 m × 0.31 mm (i.d.) glass capillary with a 0.52-μm-thick cross-linked methyl silicone stationary phase. The oven temperature was programmed from 75 to 180 °C at 20.0 °C/min and held at 180 °C for 7.5 min. The ^{63}Ni electron capture detector was operated at 325 °C.

Temperature control techniques evolved over the course of this study. In early experiments, we relied on the anaerobic chamber, itself, to serve as a buffer of short-term temperature fluctuations. Later, more precise temperature control was achieved by use of a jacketed beaker connected to a water bath outside the chamber with an immersion circulator. All experiments reported in this paper were conducted at a nominal temperature of 25 °C unless specified otherwise.

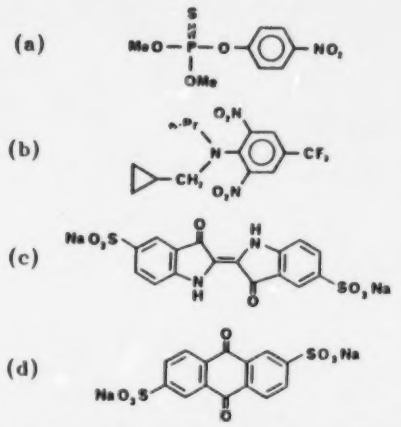

Figure 1. Structures of (a) methyl parathion, (b) profluralin, (c) indigodisulfonate, and (d) anthraquinonedisulfonate.

Sterile control experiments were performed by autoclaving all glassware, including the reductor, and preparing all solutions with 0.45 or 0.22 μm filter-sterilized water. The electrodes were rinsed briefly with 70% methanol in water at pH 1 and thereafter rinsed with and stored in sterile solutions only. To verify the absence of viable organisms, aerobic cultures (pour plates with BBL nutrient agar) and anaerobic cultures (tubes with Difco fluid thioglycolate medium) were prepared with aliquots taken from all stages of the procedure and incubated at 30 °C. A culture test was deemed negative if colonies or cloudiness did not develop in 3–5 days.

RESULTS AND DISCUSSION

Model Redox Systems. Many candidates for model systems were considered. Three based on quinone–hydroquinone redox couples were selected to model the reducing capability of polyphenolic structures that exist in natural organic matter. Other factors that are important in designing well-poised model systems are the reversibility, solubility, and electrode response of the redox couple.

The disodium salt of indigo-2,6-disulfonate (indigo carmine; Figure 1) is a dye that forms a reversible, quinone–hydroquinone redox couple. It is soluble up to about 1 g/100 mL at 25 °C, and the redox half-reaction involves both electrons and protons so indigodisulfonate can serve as an Eh poising agent and a pH buffer. Its reduction potential when half-oxidized at pH 7 (E_{m7}) is −125 mV (versus SHE), and the acid dissociation constant of the first hydroxyl of the hydroquinone form (pK_{a1}) is 7.4 (Ottaway, 1972). The disodium salt of anthraquinone-2,6-disulfonic acid (Figure 1) is a commercially available material that is functionally similar to indigodisulfonate but is more typical of the quinone and hydroquinone structures that are believed to exist in humic material. The E_{m7} of this redox couple is −84 mV, and the pK_{a1} is 8.1 (Clark, 1960). 1,4-Benzoquinone and its hydroquinone form a nonideal redox couple in aqueous solution (Chambers, 1974) that has been used by others to model the redox properties of natural organic matter (Waite, in press). The E_{m7} of this redox couple is +285 mV, and the pK_{a1} is 9.76 (Janz and Ives, 1961).

Control Studies. Several experiments were conducted that—taken together—verify that the disappearance of methyl parathion (Figure 1) was due to abiotic reduction of the nitro aromatic functional group to its amino analogue without photosensitization. In the time periods of

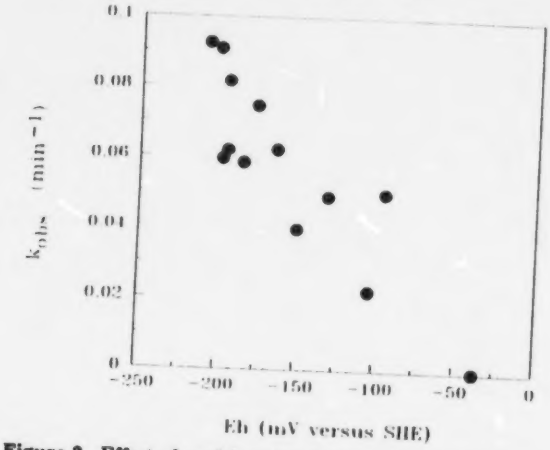

Figure 2. Effect of model system redox potential on the disappearance rate of methyl parathion in 5 mM solutions of indigodisulfonate at pH 7.0 and 25 °C.

these experiments the following were observed: (1) There was no disappearance of methyl parathion in pure water blanks, and no significant hydrolysis is expected based on the work of others using buffer solutions (Harris, 1982). (2) Fenthion (a phosphorothioate pesticide structurally similar to methyl parathion but without the reducible 4-nitro substituent) showed no disappearance in indigodisulfonate or anthraquinonedisulfonate model systems. (3) After substantial disappearance of methyl parathion in indigodisulfonate, the hydrolysis product *p*-nitrophenol was not detectable by HPLC with diode-array detection. (4) When the indigodisulfonate reaction mixture was extracted with methylene chloride (instead of isooctane), a peak that increased in size regularly with time was observed. The ratio of retention times for the product peak to methyl parathion was 0.75, which is the same as reported by Adhya et al. (1981a) for the aminomethyl parathion to methyl parathion retention time ratio. A procedure for making aminomethyl parathion by reduction of methyl parathion with chromous chloride (Forbes et al., 1975; Volpé and Mallet, 1980) produced a material that gave a mass spectrum consistent with that of aminomethyl parathion and that chromatographed with the same retention time as the product peak. (5) Dark control studies in indigodisulfonate and anthraquinonedisulfonate systems showed that ambient laboratory lighting did not affect the reaction. (6) Many of the methyl parathion in indigodisulfonate experiments were performed in sterile solutions and checked for viable organisms with aerobic and anaerobic culture techniques. The studies indicated that sterilization had no effect on the experimental results and, therefore, that the chemistry under study was, in fact, abiotic.

Indigodisulfonate. One of the goals of this research was to determine the effect of the model system Eh on the reaction rate. This was satisfactorily achieved with the indigodisulfonate system by a series of experiments all at pH 7.0 but with Eh ranging from −37 to −208 mV. These experiments showed that k_{obs} increased as Eh became more negative (Figure 2). This trend is reasonable insofar as a low Eh reflects a high concentration of reduced species in these 5 mM poised systems and the reduced indigodisulfonate is the reducing agent of methyl parathion.

Because nitro reduction involves hydrogen ions as well as electrons, it was also appropriate to investigate the effect of the model system pH on the reaction rate. Accordingly, indigodisulfonate systems were formulated at −125 mV

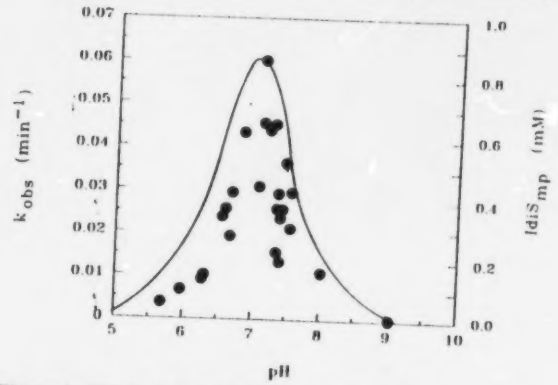

Figure 3. Effect of model system pH on the disappearance rate of methyl parathion in 5 mM solutions of indigodisulfonate at Eh −125 mV at 25 °C (points, left scale). The solid line shows the concentration of the monophenolate of indigodisulfonate calculated for Eh −125 mV and 25 °C (right scale).

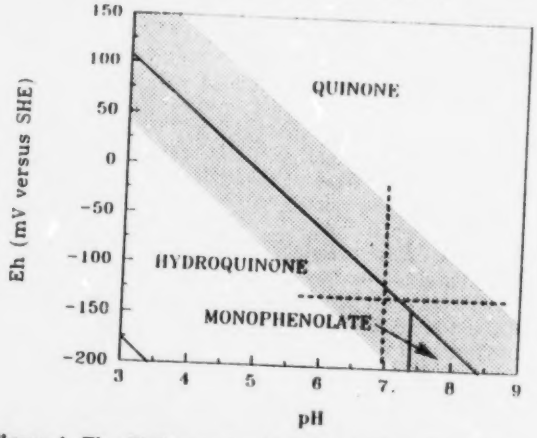

Figure 4. Eh–pH diagram for the indigodisulfonate system at 25 °C. The diagonal line in the middle of the figure divides the quinone (upper right) from the hydroquinone (lower left) fields of predominance. The shaded region marks the range of Eh–pH combinations that can be poised with an indigodisulfonate solution allowing for up to 500:1 imbalance in the quinone and hydroquinone. The triangular field in the lower-right corner is where the monophenolate of the hydroquinone is the predominant form. The dashed lines locate the range of Eh's at pH 7.0 and pH's at Eh −125 mV where disappearance studies were performed. Below and to the left of the diagonal line in the bottom-left corner is where H_2 is stable with respect to water.

over the range pH 5.68–9.03, and the rate of methyl parathion disappearance was observed. This series of experiments showed that k_{obs} has a maximum value around pH 7.1 but declines rapidly on both sides of this maximum (Figure 3).

Inspection of the Eh/pH diagram for the speciation of indigodisulfonate (Figure 4) reveals that the concentration of the hydroquinone with one of the hydroxyl groups dissociated (monophenolate form) is substantial at Eh/pH conditions at which the rate of methyl parathion reduction is fastest. The concentration of the monophenolate indigodisulfonate, $IdiS_{mp}$, can be calculated in order to check for a correlation between $IdiS_{mp}$ and k_{obs} (Tratnyek, 1987). The calculation involves eq 1, a form of the Nernst

$$Eh = E_m + (RT/2F) \ln [(C_0/C_r)([H^+]^2 + K_{a1}[H^+])] \quad (1)$$

equation, where C_0 and C_r refer to the molar concentrations

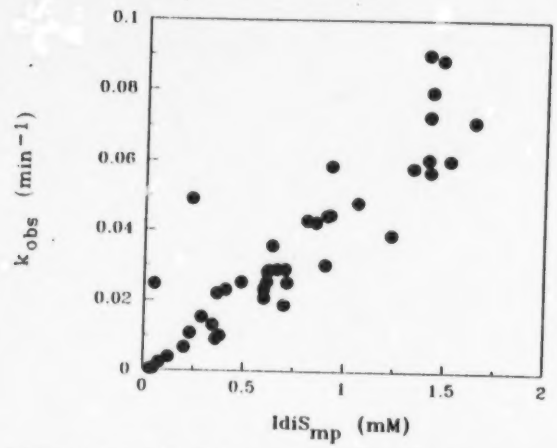

Figure 5. Correlation between the disappearance rate constant of methyl parathion and the calculated concentration of monophenolate indigodisulfonate. Total concentration of the indigodisulfonate redox couple is 5 mM and temperature is 25 °C.

of the oxidized and reduced forms, respectively, of indigodisulfonate; E_m is the formal potential at pH 0, +291 mV; and K_{r1} is the acid dissociation constant for the first hydroxyl group of the reduced form, $10^{-7.4}$ (Ottaway, 1972). This relationship is valid up to about pH 11, above which ionization of the second hydroxyl group becomes important. Equation 1 can be used to calculate $IdiS_{mp}$ as a function of pH at Eh −125 mV, and this is represented by the solid line in Figure 3. The correspondence between the curve and the data strongly suggests that the concentration of the monophenolate indigodisulfonate controls the rate of nitro reduction of methyl parathion at constant Eh.

Equation 1 can be used to calculate $IdiS_{mp}$ for all experiments in the indigodisulfonate model system, and this is plotted against k_{obs} in Figure 5. The plot appears to be linear with an intercept near zero. Visual inspection shows no trend in the dispersion: The scatter appears to be random. The coefficient of determination, r^2, between the two variables is 0.45 (using a two-parameter, linear model); that is, $IdiS_{mp}$ accounts for only 45% of the variation in k_{obs}. However, control studies have been performed to determine the amount of variability in k_{obs} that results from experimental error. A relative standard deviation of 2–7% is due to indeterminate errors in volume transfer, mixing, extraction, and analysis by gas chromatography. Four replicates of independent disappearance studies that were adjusted to the electrode readings of pH 7.0 and Eh −125 mV gave k_{obs} with a relative standard deviation of 35%. This large uncertainty is due to two things: (1) actual differences in solution chemistry despite nominal agreement in electrode readings; (2) inadequate temperature control prior to implementation of the jacketed beaker. Taken together, these control studies and $IdiS_{mp}$ account for approximately all of the variation in k_{obs} so there is no need to invoke any additional variable to predict the rate of this reaction.

This interpretation of Figure 5 leads to the conclusion that the rate of reduction of methyl parathion is first order in concentration of monophenolate indigodisulfonate as well as first order in concentration of methyl parathion (eq 2), where MeP represents methyl parathion. The monophenolate has previously been shown to be rate controlling

$$-d[MeP]/dt = k[MeP][IdiS_{mp}] \quad (2)$$

in the reduction of ferric ion by hydrobenzoquinone (Baxendale et al., 1951; Mentasti et al., 1973). Regression (using a two-parameter, linear model) on the data in Figure 5 gives a slope of 31.1 L min^{-1} mol^{-1}, which is the second-order rate constant, k, in the rate law that is eq 2. An estimate of the uncertainty in k may be obtained from the standard deviation of the slope. Assuming, for simplicity, that all the error is in k_{obs} and none in $IdiS_{mp}$, the value is 4.9 L min^{-1} mol^{-1}. This formalism indirectly relates the Eh and pH of the system to the rate of reduction of methyl parathion through the concentration of monophenolate-reduced indigodisulfonate. Such a link would be difficult to determine with experiments done in complex natural materials.

It is generally believed that the reversible oxidation–reduction of quinone systems proceeds by two one-electron steps via a semiquinone radical intermediate (Chambers, 1974), and the possible role of these highly reactive semiquinone radicals must be considered. The mathematics for including semiquinones in thermodynamic speciation calculations are described by Clark (1960). Priesler et al. (1959) have made indigodisulfonate one of the most thoroughly investigated systems with regard to the role of semiquinone radicals. They concluded that indigodisulfonate semiquinone is only a significant species (imparts a visible red color) in solutions between pH 10.5 and 12.5 (Eh −250 to −350 mV). Under the conditions used in this project, the semiquinone is always less than 5% of the total concentration of indigodisulfonate and generally much less. There is no correlation between the Eh/pH dependence of reduction rate of methyl parathion and the effect of Eh/pH on the abundance of indigodisulfonate semiquinone. For these two reasons, it is concluded that indigodisulfonate semiquinone is not controlling the kinetics of methyl parathion reduction. However, this project does not include any direct experimental investigation of the possible role of semiquinone radicals.

A short series of disappearance studies were done with profluralin (Figure 1), instead of methyl parathion, in indigodisulfonate systems (data not shown). The rate of reduction of profluralin is also apparently first order in concentration of monophenolate indigodisulfonate as well as first order in concentration of profluralin (eq 3). Regression (using a two-parameter, linear model) on the data gave a slope of 79.0 L min^{-1} mol^{-1}, which is the second-order rate constant, k, in eq 3. The uncertainty in k is reflected by the standard deviation of the slope, which is 8.6 L min^{-1} mol^{-1}.

$$-d[profluralin]/dt = k[profluralin][IdiS_{mp}] \quad (3)$$

Anthraquinonedisulfonate. In anthraquinonedisulfonate model systems at pH 6.0, the effect of Eh on the nitro reduction of methyl parathion (Figure 6) is similar to that observed in the indigodisulfonate system (Figure 2). Furthermore, the effect of pH at Eh −125 mV is analogous for anthraquinonedisulfonate (Figure 7) to that of indigodisulfonate (Figure 3).

The concentration of the monophenolate form of the anthraquinonedisulfonate system, $AQdiS_{mp}$, can be calculated in the same way as it was for the indigodisulfonate system (Tratnyek, 1987). Equation 1 was solved for C_0/C, with 228 mV for E_m and 8.1 for pK_{r1} from Clark (1960). The solid line in Figure 7 represents $AQdiS_{mp}$ as a function of pH at Eh −125 mV. As with indigodisulfonate, the correspondence between the line and the data points clearly suggests that the concentration of the monophenolate of anthraquinonedisulfonate controls the reaction rate. The plot of k_{obs} versus $AQdiS_{mp}$ (Figure 8) is analogous to Figure 5. The reduction of methyl parathion

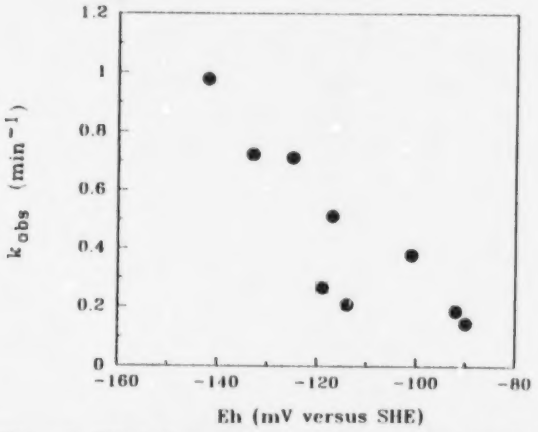

Figure 6. Effect of model system redox potential on the disappearance rate of methyl parathion in anthraquinonedisulfonate at pH 6.0 and 25 °C.

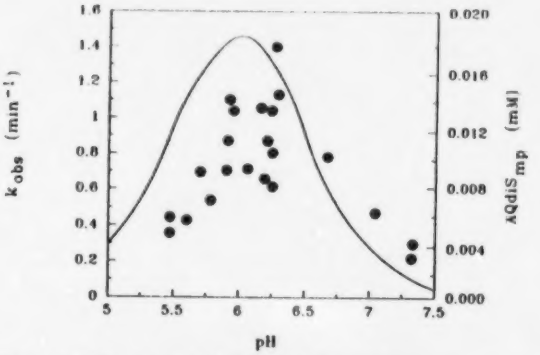

Figure 7. Effect of model system pH on the disappearance rate of methyl parathion in anthraquinonedisulfonate at Eh −125 mV and 25 °C (points, left scale). The solid line shows the concentration of the monophenolate of anthraquinonedisulfonate calculated for Eh −125 mV and 25 °C (right scale).

is first order in concentration of monophenolate anthraquinonedisulfonate as well as first order in concentration of methyl parathion so the rate law has the form of eq 4.

$$-d[MeP]/dt = k[MeP][AQdiS_{mp}] \quad (4)$$

Regression (using a two-parameter, linear model) on the data in Figure 8 gives a slope of 3.80×10^4 L min^{-1} mol^{-1}, which is the second-order rate constant, k, in the above rate law. The standard deviation of the slope is 0.65×10^4 L min^{-1} mol^{-1}.

Benzoquinone. Measured electrode potentials in benzoquinone systems that were nearly fully reduced were erratic but dramatically less so when NaCl was added. Therefore, a series of four disappearance studies were done to test the effect of salt concentration on the electrode behavior and reaction rate. The reaction medium used was 5 mM hydroquinone treated with a clean H_2/Pt reductor. The solutions were adjusted to pH 8.0, and the resulting electrode potentials were about +25 mV at WIG and about −450 mV at Pt (we suspect this discrepancy is due, in part, to the contribution of the H_2/H^+ couple catalyzed at the Pt electrode surface; Tratnyek, 1987). The reaction rate did not vary significantly over the NaCl concentration range of 1–1000 mM. A salt concentration of 10 mM was adequate to stabilize electrode response and was used in

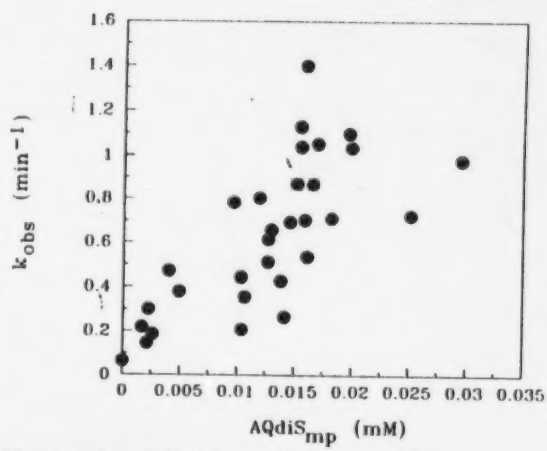

Figure 8. Correlation between the disappearance rate constant of methyl parathion and the calculated concentration of monophenolate anthraquinonedisulfonate. Total concentration of the anthraquinonedisulfonate model system is 5 mM and temperature is 25 °C.

all further disappearance studies.

In all, 22 disappearance studies were made with the benzoquinone system. In addition to the different salt concentrations, the treatments tested the effects of starting with quinhydrone instead of dihydrobenzoquinone and using the H_2/Pt reductor on the dihydrobenzoquinone. The data do not exhibit the consistent trends that were found with indigodisulfonate and anthraquinonedisulfonate systems. In fact, the rate of reaction appears to be relatively constant in systems that were exposed to the reductor regardless of the pH, measured electrode potential, or degree of H_2/Pt treatment. The first-order methyl parathion disappearance rate constant was 0.05 min^{-1} with a standard deviation of 0.02 min^{-1}. Systems that were not treated with the H_2/Pt reductor gave little or no evidence of methyl parathion disappearance: k_{obs} was less than 0.0005 min^{-1}. We suspect that Pt-catalyzed reduction by dissolved H_2 is responsible for this discrepancy, but further research will be necessary to fully interpret the results obtained in such nonideal poised systems.

Fulvic Acid. The validity of indigodisulfonate and anthraquinonedisulfonate systems as models of natural organic matter has not been demonstrated experimentally. This would be partly achieved if it were possible to document, in natural organic matter, the same rate versus Eh and pH dependence observed in the disulfonate systems. A few experiments toward this end were performed with fulvic acid, but they were inconclusive in very much the same ways as the disappearance studies in dihydrobenzoquinone with 10 mM NaCl. The electrode potentials were not erratic but were prone to drift, Pt gave lower potentials than WIG, and both measured unreasonably low when the solution was treated with a H_2/Pt reductor while the relationship to measured potential and pH remained unclear.

Apparent Reduction Potential. The reduction rate observed with the indigodisulfonate system declines quite steeply with increasing redox potential; consequently, there appears to be an Eh limit at about −50 mV above which disappearance is undetectable in 1-day experiments (Figure 2). The same trend holds for the anthraquinonedisulfonate model system (Figure 6), but the limit is about −75 mV. Experimentally this limit seems abrupt: A small increase in Eh results in a change from rates with half-lives of minutes or hours to no detectable disappearance over

many days. Similar observations have been made in natural materials: Reduction of 2,3,5,6-tetrachloronitrobenzene in anaerobic sewage sludge was rapid below about −150 mV and undetectable above that redox potential (Geer, 1978). There is also an abrupt change between +50 and +150 mV above which trifluralin showed no reduction in flooded soils (Willis et al., 1974). The Eh limits obeserved in our model system studies are operationally equivalent to the apparent reduction potential (ARP) as defined by Conant (1926). Conant coined the term to describe the irreversible reduction of an organic substrate by a homogeneous solution of redox-reversible reducing agent. The concept has been developed further by Fieser (1930) and called the critical oxidation potential. Judicious use of this terminology may help clear up some of the ambiguity regarding the relationship between redox potentials and redox reaction rates in the environmental chemistry literature.

Reducing Capability of Natural Hydroquinones. This research has shown that quinone model systems with potentials below the ARP of methyl parathion—about −50 mV under the conditions employed—will react rapidly to affect nitro reduction. The kinetics of methyl parathion disappearance and aminomethyl parathion appearance established here for model systems are similar to those observed by Wolfe et al. (1986) for a reducing sediment. Furthermore, the effect of Eh on k_{obs} they report for natural samples taken from the same site is quite similar to what we have observed in the model systems. These similarities support the presupposition that hydroquinones in natural organic matter contribute to the nitro reduction of pollutants. However, further study in model systems like benzoquinone and in fulvic acid—in addition to natural materials—is necessary to validate this hypothesis.

It seems possible, on the basis of these data, that hydroquinones contribute to the reduction of pollutants in the environment, but their role is likely to be complex. There are several possible complicating factors that require further investigation. First, the distribution of environments in which hydroquinones exist in natural organic matter may be such that some sites are much more or less strongly reducing than dihydrobenzoquinone itself. Second, there may be a critical catalytic or mediation process in natural reducing material that is destroyed by extraction of fulvic acid and/or is not provided for in the model systems. Third, other reducing agents, such as ferrous ion or its complexes, probably contribute substantially to the rapid reduction of compounds like methyl parathion in the environment so reduction due to hydroquinones may prove to be only one of several contributing pathways.

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Registry No. Methyl parathion, 298-00-0; indigodisulfonate, 483-20-5; anthraquinonedisulfonate, 53123-81-2; quinhydrone, 106-34-3; dihydroquinone, 123-31-9; profluralin, 26399-36-0.

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